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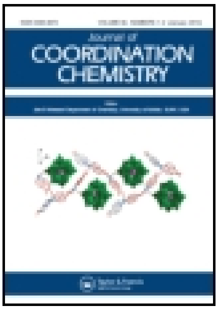

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Syntheses, characterizations, and crystal structures of 3d-s/d^{10} metal complexes derived from two compartmental Schiff base ligands

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Syntheses, characterizations, and crystal structures of 3d–s/d^{10} metal complexes derived from two compartmental Schiff base ligands

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The present investigation reports the syntheses, characterizations, and crystal structures of nine copper (II)/nickel(II)–s/d^{10} complexes, $[Cu^{II}L^{1}Na^{I}(ClO_4)(CH_3CN)]$ (**1**), $[Cu^{II}L^{1}K^{I}(ClO_4)(CH_3COCH_3)]$ (**2**), $[Cu^{II}L^{2}Zn^{II}Cl_2]\cdot CH_3CN$ (**3**), $[(Cu^{II}L^{2})_2Na^{I}](ClO_4)\cdot CH_3COCH_3$ (**4**), $[(Ni^{II}L^{1})_2K^{I}](ClO_4)$ (**5**), $[(Cu^{II}L^{1})_2Cs^{I}(ClO_4)]\cdot 2CH_3CN$ (**6**), $[(Ni^{II}L^{1})_2Cs^{I}(ClO_4)]\cdot 2H_2O$ (**7**), $[(Cu^{II}L^{2})_2Sr^{II}(H_2O)_2](NO_3)_2$ (**8**), and $[\{Cu^{II}L^{2}Li^{I}(H_2O)\}_2(\mu\text{-}H_2O)](ClO_4)_2$ (**9**), where H_2L^1 and H_2L^2 are two 3-methoxysalicylaldehyde-diamine (H_2L^{OMe}) ligands in which the diamine moieties are *o*-phenylenediamine and *trans*-1,2-diaminocyclohexane, respectively. Among these nine compounds, three (**1**, **2**, and **3**) are dinuclear, five (**4**, **5**, **6**, **7**, and **8**) are trinuclear, and **9** is tetranuclear. Trinuclear **6** and **7** are double-decker sandwich systems. Some (in **3** and **9**) or all (in **1**, **2**, and **4–8**) of the four oxygens of the $O(phenoxo)_2O(methoxy)_2$ compartment(s) are coordinated to the second metal ion (Na^I in **1** and **4**, K^I in **2** and **5**, Zn^{II} in **3**, Cs^I in **6** and **7**, Sr^{II} in **8**, and Li^I in **9**). The di/tri/tetranuclear molecules in **2–9** are self-assembled by weak attractions, such as hydrogen bonds/cation $(K^I)\cdots\pi$/C–H$\cdots\pi$ interactions. The following self-assemblies are observed: 1-D in **3**, **7**, and **9**, 1-D ladder in **4**, 2-D in **8**, and 3-D in **2** and **5**.

Keywords: Heterometallic; Compartmental ligands; Self-assemblies; s-Block metal ions; Double-decker

1. Introduction

Preorganized dinucleating ligands are important for designed syntheses of homo/heterometallic systems [1–7]. Compartmental dinucleating ligands are those in which the two compartments are dissimilar regarding donor centers (*e.g.* 2:1 condensation product of 3-methoxy [5–22]/ethoxy [23–31]/carboxylate [1] salicylaldehyde and a diamine) or similar regarding the donor centers but dissimilar structurally (*e.g.* 2:1:1 condensation product of 4-methyl-2,6-diformylphenol, 1,3-propane diamine, and ethylenediamine) [32]. Although both homometallic and heterometallic systems can be derived from compartmental ligands, as these ligands stabilize heterometallic systems.

3-Methoxysalicylaldehyde-diamine (H_2L^{OMe}) and 3-ethoxysalicylaldehyde-diamine (H_2L^{OEt}) Schiff bases are compartmental ligands containing two dissimilar sets of donor centers, one N_2O_2 and another O_4 [5–31]. The N_2O_2 compartment has potential to accommodate a 3d metal ion, which on reaction with a second metal salt produces homo/

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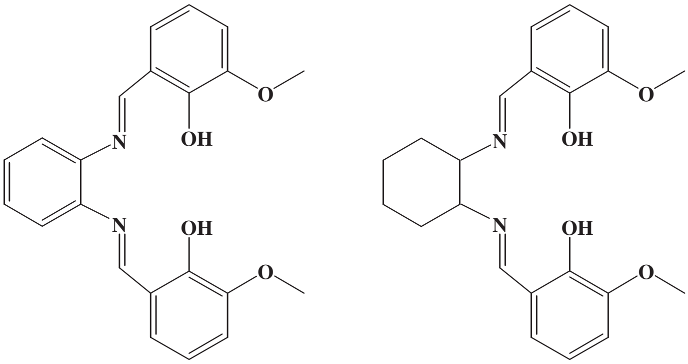

H_2L^1 H_2L^2

Chart 1. Chemical structures of H_2L^1 and H_2L^2.

heterometallic systems. In addition to dinuclear compounds, these ligands can produce oligonuclear and polymeric systems even in the absence of a secondary bridging ligand because of the coordination of one O_4 compartment to more than one metal ion. As the O_4 compartment can coordinate with various types of metal ions, di/oligo/polynuclear systems of metal ion combinations 3d–s/p/d/d^{10}/f have been reported [5–31]. Some of these compounds are examples of two-component and even three-component cocrystals [13,23–31]. To explore the heterometallic 3d–s/d^{10} complexes derived from N_2O_2–O_4 compartmental ligands, we have reacted mononuclear copper(II)/nickel(II) complexes derived from two H_2L^{OMe} ligands, H_2L^1 and H_2L^2 (Chart 1), with Li^IClO_4/Na^IClO_4/K^IClO_4/Cs^IClO_4/$Sr^{II}(NO_3)_2$/$Zn^{II}Cl_2$ and isolated nine heterometallic systems, $[Cu^{II}L^1Na^I(ClO_4)(CH_3CN)]$ (**1**), $[Cu^{II}L^1K^I(ClO_4)(CH_3COCH_3)]$ (**2**), $[Cu^{II}L^2Zn^{II}Cl_2]\cdot CH_3CN$ (**3**), $[(Cu^{II}L^2)_2Na^I](ClO_4)\cdot CH_3COCH_3$ (**4**), $[(Ni^{II}L^1)_2K^I](ClO_4)$ (**5**), $[(Cu^{II}L^1)_2Cs^I(ClO_4)]\cdot 2CH_3CN$ (**6**), $[(Ni^{II}L^1)_2Cs^I(ClO_4)]\cdot 2H_2O$ (**7**), $[(Cu^{II}L^2)_2Sr^{II}(H_2O)_2](NO_3)_2$ (**8**), and $[\{Cu^{II}L^2Li^I(H_2O)\}_2(\mu\text{-}H_2O)](ClO_4)_2$ (**9**), where H_2L^1 and H_2L^2 are the two 3-methoxysalicylaldehyde-diamine (H_2L^{OMe}) ligands in which the diamine moieties are *o*-phenylenediamine and *trans*-1,2-diaminocyclohexane (Chart 1), respectively. Herein, we report the syntheses, characterizations, and crystal structures of these nine heterometallic systems.

2. Experimental

Caution! Perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared and it should be handled with caution.

2.1. *Materials and physical methods*

All reagents and solvents were purchased from commercial sources and used as received. $[Cu^{II}L^2\subset(H_2O)]$ [13], $[Cu^{II}L^1\subset(H_2O)]$, and $[Ni^{II}L^1\subset(H_2O)]$ were synthesized by reacting H_2L^1 or H_2L^2 with copper(II)/nickel(II) acetate in methanol–water according to reported procedure for this type of system [12,13]. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded from KBr disks (400–4000 cm^{-1}) on a Bruker-Optics Alpha–T spectrophotometer.

2.2. *Syntheses of 1–9*

These nine compounds were prepared by reacting one of the three mononuclear compounds $[Cu^{II}L^{2}\subset(H_2O)]$ (for **3**, **4**, **8**, and **9**), $[Cu^{II}L^{1}\subset(H_2O)]$ (for **1**, **2**, and **6**) and $[Ni^{II}L^{1}\subset(H_2O)]$ (for **5** and **7**) with appropriate salts of metal ions. The salts used are: $NaClO_4{\cdot}H_2O$ for **1** and **4**, $KClO_4$ for **2** and **5**, $ZnCl_2$ for **3**, $CsClO_4$ for **6** and **7**, $Sr(NO_3)_2$ for **8**, and $LiClO_4{\cdot}3H_2O$ for **9**. For **1–4**, **6**, **7**, and **8**, a suspension of $[Cu^{II}L^{2}{}_{(H_2O)}]/[Cu^{II}L^{1}{}_{(H_2O)}]/[Ni^{II}L^{1}{}_{(H_2O)}]$ in a solvent (acetonitrile for **1**, **3**, **6**, and **8** and acetone for **2**, **4**, and **7**) was treated with a solution of the metal salt in the same (acetonitrile for **1**, **3**, and **6** and acetone for **2**, **4**, and **7**) or a different (water for **8**) solvent to result in a red (for **1–4**, **6–8**) or orange (for **3**) solution from which the product was isolated. For **5** and **9**, a suspension of $[Cu^{II}L^{2}\subset(H_2O)]/[Ni^{II}L^{1}\subset(H_2O)]$ in dichloromethane was treated with a solution of $LiClO_4{\cdot}3H_2O/KClO_4$ in acetonitrile and then diethylether was diffused slowly to the resulting red solution to generate the compounds. As representative examples for the two sets, syntheses of **7** and **9** are described.

An acetone solution (5 mL) of $CsClO_4$ (0.051 g, 0.22 mmol) was added dropwise to a suspension of $[Ni^{II}L^{1}\subset(H_2O)]$ (0.100 g, 0.22 mmol) in acetone (15 mL) under stirring. After stirring for half an hour, the dark red solution was filtered to remove any suspended particles and the filtrate was kept at room temperature and allowed to evaporate slowly. After a few days, dark red crystalline **7**, containing diffraction quality single crystals, deposited were collected by filtration and washed with cold acetone. The crystals lost solvent after isolation (*vide infra*). Yield: 0.098 g (79%). Anal. Calcd for $C_{44}H_{40}N_4O_{14}ClNi_2Cs$: C, 46.58; H, 3.56; N, 7.06. Found: C, 46.46; H, 3.67; N, 7.00. IR (cm^{-1}, KBr): $\nu(H_2O)$, 3443 m; ν(C–H), 3052 w, 2931 w, 2831 w; ν(C=N), 1606 vs; $\nu(ClO_4)$, 1102 s, 1080 s, 621 w.

An acetonitrile solution (3 mL) of $LiClO_4{\cdot}3H_2O$ (0.035 g, 0.22 mmol) was added dropwise to a suspension of $[Cu^{II}L^{2}\subset(H_2O)]$ (0.100 g 0.22 mmol) in dichloromethane (5 mL) under stirring. After stirring for half an hour, the red solution was filtered to remove any suspended particles. Then diethylether was allowed to diffuse slowly to the filtrate in a long tube. After *ca*. 10 days, a red crystalline compound, containing diffraction quality single crystals of **9** deposited, were collected by filtration and washed with cold methanol. Yield: 0.076 g (60%) Anal. Calcd for $C_{44}H_{54}N_4O_{19}Cl_2Cu_2Li_2$: C, 45.76; H, 4.71; N, 4.85. Found: C, 45.94; H, 4.62; N, 4.97. IR (cm^{-1}, KBr): $\nu(H_2O)$, 3451 m; ν(C–H), 3052 w, 2937 m, 2852 w; ν(C=N), 1635 vs; $\nu(ClO_4)$, 1080 s, 624 w.

Data for **1**: Color: red. Yield: 0.112 g (85%). Anal. Calcd for $C_{24}H_{21}N_3O_8ClCuNa$: C, 47.93; H, 3.52; N, 6.99. Found: C, 47.78; H, 3.63; N, 6.86. IR (cm^{-1}, KBr): ν(C–H), 3051 w, 2925 w, 2835 w; ν(C=N), 1608 vs; $\nu(ClO_4)$, 1108 s, 1060 m, 625 w; ν(acetonitrile), 2284 w.

Data for **2**: Color: red. Yield: 0.105 g (75%). Anal. Calcd for $C_{25}H_{24}N_2O_9ClCuK$: C, 47.32; H, 3.81; N, 4.42. Found: C, 47.48; H, 3.84; N, 4.32. IR (cm^{-1}, KBr): ν(C–H), 3057 w, 2932 w, 2840 w; ν(C=N), 1608 vs; $\nu(ClO_4)$, 1110 s, 1084 s, 627 m; ν(acetone), 1701 w.

Data for **3**: Color: red. Yield: 0.089 g (65%). Anal. Calcd for $C_{24}H_{27}N_3O_4Cl_2CuZn$: C, 46.39; H, 4.38; N, 6.76. Found: C, 46.28; H, 4.30; N, 6.84. IR (cm^{-1}, KBr): ν(C–H), 3056 w, 2933 w, 2857 w; ν(C=N), 1629 vs.

Data for **4**: Color: red. Yield: 0.094 g (80%). Anal. Calcd for $C_{47}H_{54}N_4O_{13}ClCu_2Na$: C, 52.83; H, 5.09; N, 5.24. Found: C, 52.67; H, 5.14; N, 5.12. IR (cm^{-1}, KBr): ν(C–H), 3055 w, 2934 m, 2860 w; ν(C=N), 1629 vs; $\nu(ClO_4)$, 1088 vs, 623 m; ν(acetone), 1707 m.

Data for **5**: Color: red. Yield: 0.064 g (58%). Anal. Calcd for $C_{44}H_{36}N_4O_{12}ClNi_2K$: C, 52.60; H, 3.61; N, 5.58. Found: C, 52.71; H, 3.54; N, 5.69. IR (cm^{-1}, KBr): ν(C–H), 3055 w, 2966 w, 2927 w, 2836 w; ν(C=N), 1607 vs; $\nu(ClO_4)$, 1091 s, 624 w.

Data for **6**: Color: red. Yield: 0.115 g (88%). Anal. Calcd for $C_{48}H_{42}N_6O_{12}ClCu_2Cs$: C, 48.43; H, 3.56; N, 7.06. Found: C, 48.59; H, 3.64; N, 7.18. IR (cm^{-1}, KBr): *ν*(C–H), 3053 w, 2926 w, 2832 w; *ν*(C=N), 1608 vs; *ν*(ClO_4), 1082 vs, 622 w.

Data for **8**: Color: red. Yield: 0.102 g (82%). Anal. Calcd for $C_{44}H_{52}N_6O_{16}Cu_2Sr$: C, 46.54; H, 4.62; N, 7.40. Found: C, 46.41; H, 4.65; N, 7.55. IR (cm^{-1}, KBr): *ν*(H_2O), 3638 w, 3416 m; *ν*(C–H), 3048 w, 2932 m, 2852 w; *ν*(C=N), 1638 s; *ν*(nitrate), 1379 vs, 855 m.

2.3. *Crystal structure determination of 1–9*

Crystallographic data for the nine compounds are summarized in table 1. Diffraction data of **1–9** were collected on a Bruker-APEX II SMART CCD diffractometer at 296 K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Compound **7** lost crystalline nature from loss of solvent immediately after isolation and, therefore, diffraction data of **7** were collected on mounting a crystal dipped in its mother liquor in a capillary.

The intensity data were processed with SAINT [33] and SADABS [34] and corrected for absorption effects. The crystal structures were determined by direct methods and subsequent Fourier and difference Fourier syntheses followed by full-matrix least-squares refinements on F^2 using SHELXTL [35] and SHELXTL-97 [36] packages. During refinement of the structures, some oxygens of perchlorate in **1** (O7), **2** (O5 and O7), **6** (O9, O10 and O11), **7** (O9), and **9** (O8 and O9) and Li1 in **9** were disordered over two or three sites. These disorders were modeled by allowing each to refine freely and setting sum of their occupancies to be equal to one. The final linked occupancy parameters for the atoms disordered over two sites are 0.50 and 0.50 for O7 in **1**, O5 in **2**, and Li1 in **9**; 0.60 and 0.40 for O7 in **2** and O10 and O11 in **6**; 0.80 and 0.20 for O9 in **6**; 0.90 and 0.10 for O9 in **7**; 0.83 and 0.17 for O8 in **9**. O9 of **9** was disordered over three positions and occupancies of these sites are 0.60, 0.30, and 0.10. In **2**, the minor component O7B is coordinated to the metal center, where the major component O7A remains noncoordinated [28].

The two hydrogens of water in $Cu^{II}_2Sr^{II}$ of **8** were located from difference Fourier maps. The six hydrogens of three waters in **9** were not located from Fourier difference maps and therefore these hydrogens were not considered in the refinement. The six hydrogens of solvated acetone in **4** were not located and it became problematic to insert them and therefore these six hydrogens were not considered in the refinement. All the other hydrogens in **1–9** were inserted on geometrical calculated positions with fixed thermal parameters.

The following bond distances were restrained to get better refinement: C47–C48 and C47–N6 of acetonitrile in **6** were restrained to 1.4 and 1.2 Å, respectively; Cl1–O9A bond distance in **6** was restrained to 1.37 Å; C45–C46 and C45–C47 of acetone in **4** were restrained to 1.35 Å; O9A–O11 of the perchlorate in **7** was restrained to 2.2 Å and the O–H distance of water in **8** (two molecules in this molecule are symmetry related) was restrained to 0.85 Å.

Some oxygens of perchlorate (O10B and O11B in **6**, O9B in **7**, and O8B in **9**) had to be refined isotropically because of nonpositive problems. All other nonhydrogen atoms were refined anisotropically. All hydrogens which were either located or inserted were refined isotropically.

It was not possible to assign properly all or some solvent molecules in **7** and therefore these solvent molecules were eliminated by using the SQUEEZE facility of PLATON to improve the refinement [37]. Electron count per unit cell for the eliminated solvent is 85, indicating the possibility of two acetone and two waters. However, only the two waters of

Table 1. Crystallographic data of **1–9**.

Compound no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{24}H_{21}N_3O_8ClCuNa$	$C_{25}H_{24}N_2O_9ClCuK$	$C_{24}H_{27}N_3O_4Cl_2CuZn$	$C_{47}H_{48}N_4O_{13}ClCu_2Na$	$C_{44}H_{36}N_4O_{12}ClNi_2K$	$C_{48}H_{42}N_6O_{12}ClCu_2Cs$	$C_{44}H_{36}N_4O_{12}ClNi_2Cs$	$C_{44}H_{52}N_6O_{16}Cu_2Sr$	$C_{44}H_{48}N_4O_{19}Cl_2Cu_2Li_2$
Formula weight	601.42	634.55	621.30	1062.41	1004.74	1190.32	1098.55	1135.62	1148.72
Crystal color	Red	Red	Red	Red	Red	Red	Dark red	Red	Red
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pca2_1$	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
a (Å)	12.0014(16)	7.7402(3)	8.9245(18)	11.942(3)	19.5080(7)	13.6196(4)	14.033(3)	27.2704(16)	10.1205(17)
b (Å)	16.872(2)	12.8127(5)	23.716(5)	13.229(4)	12.1406(5)	24.2777(7)	14.122(3)	7.2927(4)	11.0416(18)
c (Å)	16.5761(17)	26.6462(11)	12.866(3)	16.325(5)	17.7094(7)	14.4048(5)	25.468(4)	25.2213(15)	12.210(2)
α (°)	90.00	90.00	90.00	69.193(4)	90.00	90.00	90.00	90.00	81.426(7)
β (°)	132.054(6)	94.275(2)	106.009(2)	83.686(4)	90.00	92.8800(10)	118.581(9)	115.152(2)	69.394(6)
γ (°)	90.00	90.00	90.00	85.156(4)	90.00	90.00	90.00	90.00	71.216(6)
V (Å^3)	2492.2(5)	2635.23(18)	2617.5(9)	2393.5(12)	4194.3(3)	4757.0(3)	4432.1(15)	4540.3(5)	1208.2(3)
Z	4	4	4	2	4	4	4	4	1
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
2θ (°)	4.10–48.84	3.06–56	3.44–52.04	2.68–50.42	3.36–50.68	3.00–52.76	3.30–50.5	3.30–54.82	3.56–55.00
μ (mm^{-1})	1.056	1.145	1.968	1.022	1.132	1.775	1.787	2.179	1.072
$\rho_{calc.}$ (gcm^{-3})	1.603	1.599	1.577	1.474	1.591	1.662	1.646	1.661	1.579
F(000)	1228	1300	1268	1096	2060	2392	2208	2328	590
Abs. correction	Multi scan	Multi scan	Multi scan	Multi scan	Multi scan	Multi scan	Multi scan	Multi scan	Multi scan
Index ranges	$-13 \le h \ge 12$	$-10 \le h \ge 9$	$-10 \le h \ge 10$	$-14 \le h \ge 13$	$-22 \le h \ge 21$	$-17 \le h \ge 16$	$-16 \le h \ge 16$	$-34 \le h \ge 35$	$-13 \le h \ge 13$
	$-19 \le k \ge 19$	$-15 \le k \ge 16$	$-28 \le k \ge 28$	$-15 \le k \ge 15$	$-14 \le k \ge 14$	$-29 \le k \ge 29$	$-16 \le k \ge 16$	$-9 \le k \ge 8$	$-13 \le k \ge 14$
	$-19 \le l \ge 19$	$-35 \le l \ge 35$	$-15 \le l \ge 15$	$-19 \le l \ge 19$	$-20 \le l \ge 20$	$-17 \le l \ge 18$	$-27 \le l \ge 30$	$-32 \le l \ge 32$	$-15 \le l \ge 15$
Reflections collected	30631	33757	19420	17461	46339	57121	29488	28426	14296
Independent refl./R_{int}	4099/0.0382	6229/0.0351	5065/0.0320	8530/0.0507	7549/0.0615	9635/0.0574	7912/0.0653	5150/0.0451	5452/0.0211
R_1[a]/wR_2[b] [$I > 2\sigma(I)$]	0.0291/0.0712	0.0389/0.0743	0.0315/0.0814	0.0622/0.1243	0.0468/0.0878	0.0366/0.0812	0.0439/0.0824	0.0318/0.0842	0.0422/0.0933
R_1[a]/wR_2[b] (all Fo^2)	0.0379/0.0768	0.0579/0.0820	0.0454/0.0900	0.1310/0.1518	0.0654/0.0949	0.0618/0.0911	0.0777/0.0900	0.0526/0.0972	0.0480/0.0973

[a] $R1 = [\Sigma||Fo|-|Fc||/\Sigma|Fo|]$.

[b] $wR2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo4]^{1/2}$.

the squeezed four solvent molecules were considered in the formula, $[(Ni^{II}L^1)_2Cs^I(ClO_4)]\cdot 2H_2O$, of **7** because the crystals lost solvent (*vide supra*) and the elemental analyses are matched with a formula containing only two waters as solvents of crystallization.

The refinements converged to R_1 values $[I > 2\ \sigma(I)]$ of 0.0291, 0.0389, 0.0315, 0.0622, 0.0468, 0.0366, 0.0439, 0.0318 and 0.0422 for **1–9**, respectively.

3. Results and discussion

3.1. *Syntheses and characterization*

Compounds **1–9** were prepared by reacting the corresponding mononuclear compound with second metal salt in a single solvent or in a mixture of solvents. The solvent or mixture of solvents was selected so that the resulting compound is formed in highly crystalline form. For **5** and **9**, diethylether was diffused into the mixture of the reactants in mixture of two solvents, otherwise only powders were precipitated.

These compounds were characterized by FT-IR spectroscopy and elemental analyses. The C=N stretching frequency appears from 1606–1638 cm^{-1} as a strong band. The presence of perchlorate in **1**, **2**, **4**, **5**, **6**, **7**, and **9** was evident from a very strong band at 1060–1110 cm^{-1} and a weak band at 621–627 cm^{-1}. One strong band at 1379 cm^{-1} and a medium band at 855 cm^{-1} in the spectrum of **8** arise from nitrate. Coordinated acetonitrile in **1** is characterized by a weak band at 2284 cm^{-1}. The ketonic vibration of coordinated acetone in **2** and **4** appears at 1701 and 1707 cm^{-1} as a weak and medium intensity band, respectively.

3.2. *Description of the structures of 1–9*

The structures of **1–9** contain one or two deprotonated ligands $[L^1]^{2-}/[L^2]^{2-}$; $[L^1]^{2-}$ in **1**, **2**, **5–7** and $[L^2]^{2-}$ in **3**, **4**, **8**, and **9**. The N(imine)$_2$O(phenoxo)$_2$ compartment of each of $[L^1]^{2-}/[L^2]^{2-}$ is occupied by a copper(II) in **1–4**, **6**, **8**, and **9** and a nickel(II) in **5** and **7** as mononuclear species, $[Cu^{II}L^1]/[Ni^{II}L^1]/[Cu^{II}L^2]$. On the other hand, some or all of the four oxygens of the O(phenoxo)$_2$O(methoxy)$_2$ compartment(s) of one or more $[L^1]^{2-}/[L^2]^{2-}$ in **1–9** are coordinated with the following metal ions: Na^I in **1** and **4**; Zn^{II} in **3**; K^I in **2** and **5**;

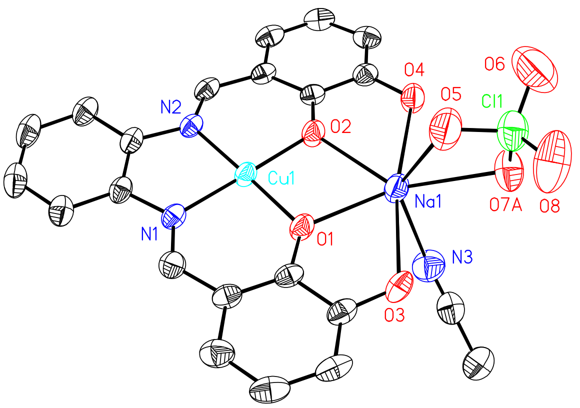

Figure 1. Crystal structure (35% thermal ellipsoids) of $[Cu^{II}L^1Na^I(ClO_4)(CH_3CN)]$ (**1**). Hydrogens, methoxy carbons and O7B of the two sites of the disordered perchlorate oxygen are omitted for clarity.

Cs^{I} in **6** and **7**; Sr^{II} in **8**; Li^{I} in **9**. Two phenoxo and two methoxy oxygens for a particular $O(phenoxo)_2O(methoxy)_2$ compartment in all these compounds form a plane as evidenced by the small mean deviations, $\leqslant 0.13$ Å, of the constituted atoms from the corresponding least-squares O_4 plane.

The structures reveal that the copper(II)–sodium(I) compound $[Cu^{II}L^{1}Na^{I}(ClO_4)(CH_3CN)]$ (**1**; figure 1), copper(II)–potassium(I) compound $[Cu^{II}L^{1}K^{I}(ClO_4)(CH_3COCH_3)]$ (**2**; figure 2), and copper(II)–zinc(II) compound $[Cu^{II}L^{2}Zn^{II}Cl_2]\cdot CH_3CN$ (**3**; figure 3) are diphenoxo-bridged dinuclear systems. However, while sodium(I) in **1** and potassium(I) in **2** are coordinated to all four oxygens of the corresponding $O(phenoxo)_2O(methoxy)_2$

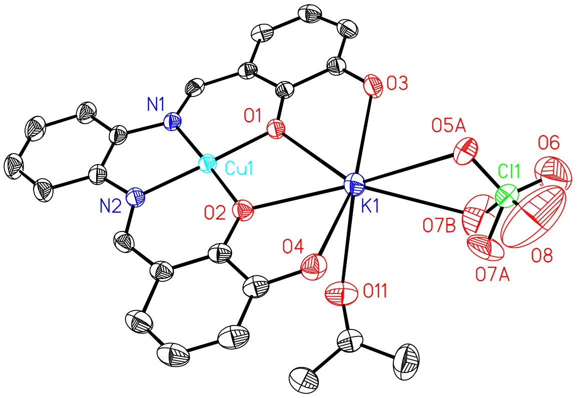

Figure 2. Crystal structure (25% thermal ellipsoids) of $[Cu^{II}L^{1}K^{I}(ClO_4)(CH_3COCH_3)]$ (**2**). Hydrogens and methoxy carbons are omitted for clarity. Both the sites (O7A and O7B) of one disordered perchlorate oxygen are shown because the site of minor occupancy is bonded with a metal ion; O5B of the two sites of the second disordered perchlorate oxygen is omitted for clarity.

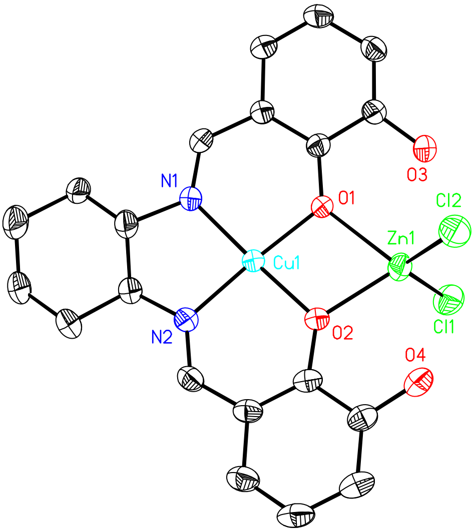

Figure 3. Crystal structure (35% thermal ellipsoids) of $[Cu^{II}L^{2}Zn^{II}Cl_2]\cdot CH_3CN$ (**3**). Hydrogens, methoxy carbons, and acetonitrile are not shown.

compartment, only the two bridging phenoxo oxygens of the corresponding O_4 compartment in **3** are coordinated to the zinc(II) center. Both the sodium(I) center in **1** and potassium(I) center in **2** are seven-coordinate, while the zinc(II) center in **3** is four-coordinate. Two of the three additional coordination positions for sodium(I) in **1** and potassium(I) in **2** are satisfied by two oxygens of a chelating perchlorate, while the third additional coordination position for sodium(I) and potassium(I) are satisfied by an acetonitrile nitrogen and acetone oxygen, respectively; both additional coordination positions for the zinc(II) center in **3** are occupied by two chlorides.

Of the nine compounds, five are trinuclear systems, copper(II)–sodium(I) compound $[(\mathrm{Cu^{II}L^2})_2\mathrm{Na^I}](\mathrm{ClO_4})\cdot\mathrm{CH_3COCH_3}$ (**4**; figure 4), copper(II)–potassium(I) compound $[(\mathrm{Ni^{II}L^1})_2\mathrm{K^I}](\mathrm{ClO_4})$ (**5**; figure 5), copper(II)/nickel(II)–cesium(I) compounds $[(\mathrm{Cu^{II}L^1})_2\mathrm{Cs^I}(\mathrm{ClO_4})]\cdot2\mathrm{CH_3CN}$ (**6**; figure 6) and $[(\mathrm{Ni^{II}L^1})_2\mathrm{Cs^I}(\mathrm{ClO_4})]\cdot2\mathrm{H_2O}$ (**7**; figure 7) and copper (II)–strontium(II) compound $[(\mathrm{Cu^{II}L^2})_2\mathrm{Sr^{II}}(\mathrm{H_2O})_2](\mathrm{NO_3})_2$ (**8**; figure 8). In these five compounds, the second metal center ($\mathrm{Na^I}$ in **4**, $\mathrm{K^I}$ in **5**, $\mathrm{Cs^I}$ in **6** and **7**, and $\mathrm{Sr^{II}}$ in **8**) is coordinated to all four oxygens of two mononuclear copper(II)/nickel(II) moieties. Thus, the second metal center resides between two mononuclear copper(II)/nickel(II) moieties and eight coordination positions of the second metal center are satisfied by the two Schiff base ligands. While the sodium(I) center in **4** and potassium(I) center in **5** are coordinated only

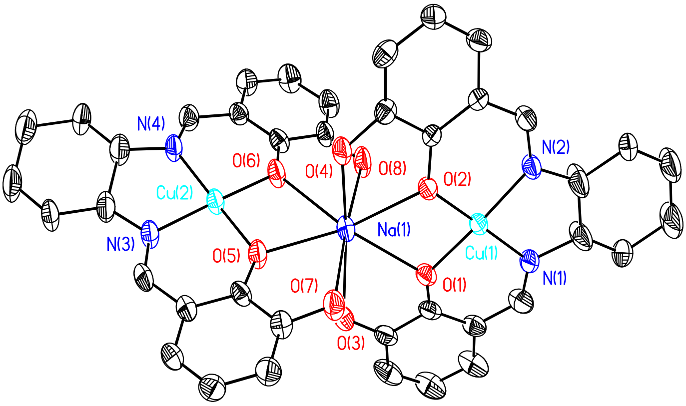

Figure 4. Crystal structure (25% thermal ellipsoids) of $[(\mathrm{Cu^{II}L^2})^2\mathrm{Na^I}](\mathrm{ClO_4})\cdot\mathrm{CH_3COCH_3}$ (**4**). Hydrogens, methoxy carbons, perchlorate, and acetone are omitted for clarity.

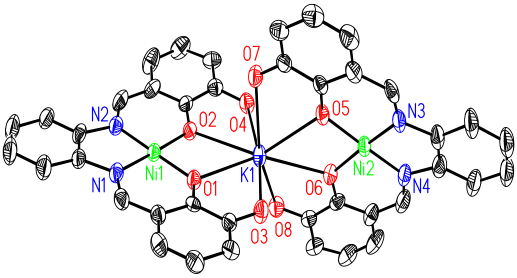

Figure 5. Crystal structure (15% thermal ellipsoids) of $[(\mathrm{Ni^{II}L^1})_2\mathrm{K^I}](\mathrm{ClO_4})$ (**5**). Hydrogens, methoxy carbons, and perchlorate are omitted for clarity.

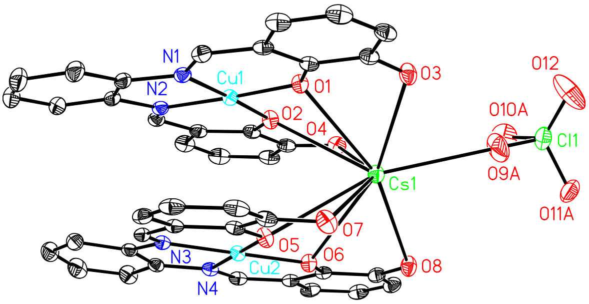

Figure 6. Crystal structure (15% thermal ellipsoids) of $[(Cu^{II}L^1)_2Cs^I(ClO_4)]\cdot 2CH_3CN$ (**6**). Hydrogens, methoxy carbons, and one (O9B, O10B and O11B) of the two sites of the three disordered perchlorate oxygens are omitted for clarity.

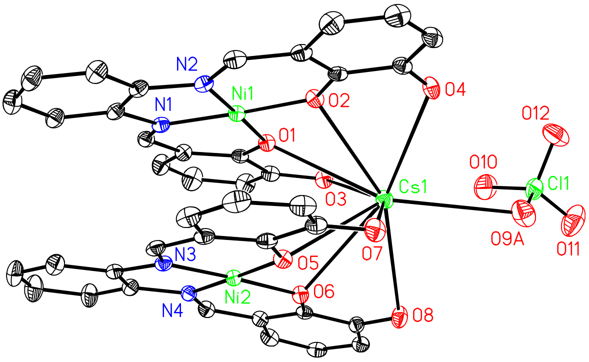

Figure 7. Crystal structure (20% thermal ellipsoids) of $[(Ni^{II}L^1)_2Cs^I(ClO_4)]\cdot 2H_2O$ (**7**). Hydrogens, methoxy carbons, and O9B of the two sites of the disordered perchlorate are omitted methoxy carbons and O9B of the two sites of the disordered perchlorate are omitted for clarity.

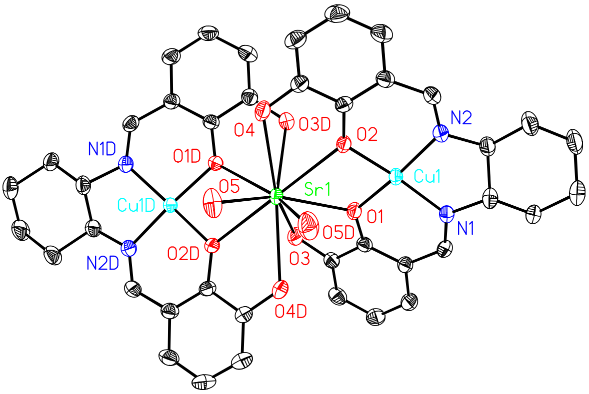

Figure 8. Crystal structure (25% ellipsoids) of $[(Cu^{II}L^2)_2Sr^{II}(H_2O)_2](NO_3)_2$ (**8**). Hydrogens, methoxy carbons, and two nitrates are omitted for clarity. Symmetry code: D, 2 − x, y, 0.5 − z.

to the Schiff bases and are thus eight-coordinate, the cesium(I) center in **6** and **7** and strontium(II) center in **8** are additionally coordinated to other donors; one oxygen of a monodentate perchlorate to Cs^{I} in **6** and **7** and two oxygens of two waters to $\mathrm{Sr}^{\mathrm{II}}$ in **8**. Thus, the Cs^{I} center in **6** and **7** are nine-coordinate, while the $\mathrm{Sr}^{\mathrm{II}}$ center in **8** is ten-coordinate.

Although **4**, **5**, **6**, **7**, and **8** are trinuclear, topologically the complexes belong to three different types. The $\mathrm{Cu}_2^{\mathrm{II}}\mathrm{Na}^{\mathrm{I}}$ (**4**) and $\mathrm{Ni}_2^{\mathrm{II}}\mathrm{K}^{\mathrm{I}}$ (**5**) compounds are similar. The second metal ion in these two cases lies almost on one O_4 plane (displacement is 0.07 Å for Na^{I} in **4** and 0.04 Å for K^{I} in **5**) and displaced by a small extent from another O_4 plane (displacement is 0.31 Å for Na^{I} in **4** and 0.44 Å for K^{I} in **5**) and the two O_4 planes are not parallel; the dihedral angle between the two least-squares O_4 planes is 89.2° for **4** and 73.9° for **5**. The $\mathrm{Cu}_2^{\mathrm{II}}\mathrm{Sr}^{\mathrm{II}}$ (**8**) compound belongs to a different type. In this case, the $\mathrm{Sr}^{\mathrm{II}}$ center is displaced by significant extent from both the O_4 planes (0.90 Å from both O_4 planes) but the two O_4 planes here are also far from being parallel; the dihedral angle between the two least-squares O_4 planes is 64.8°. In contrast, in the $\mathrm{Cu}_2^{\mathrm{II}}\mathrm{Cs}^{\mathrm{I}}$ (**6**) and $\mathrm{Ni}_2^{\mathrm{II}}\mathrm{Cs}^{\mathrm{I}}$ (**7**) compounds, the Cs^{I} center is displaced more significantly from both the two O_4 planes (displacement values are 1.56 and 1.77 Å in **6** and 1.63 and 1.96 Å in **7**) and, moreover, the two O_4 planes are almost parallel; the dihedral angle between the two least-squares O_4 planes is 2.6° in **6** and 6.1° in **7**. Evidently, while the $\mathrm{Cu}_2^{\mathrm{II}}\mathrm{Cs}^{\mathrm{I}}$ (**6**) and $\mathrm{Ni}_2^{\mathrm{II}}\mathrm{Cs}^{\mathrm{I}}$ (**7**) compounds are sandwich systems, the other three are not so.

The copper(II)–lithium(I) compound $[\{\mathrm{Cu}^{\mathrm{II}}\mathrm{L}^2\mathrm{Li}^{\mathrm{I}}(\mathrm{H_2O})\}_2(\mu\text{-}\mathrm{H_2O})](\mathrm{ClO_4})_2$ (**9**; figure 9) is a tetranuclear system in which the two lithium(I) centers of two monophenoxo-bridged $[\mathrm{Cu}^{\mathrm{II}}\mathrm{L}^2\mathrm{Li}^{\mathrm{I}}(\mathrm{H_2O})]^+$ units are bridged by water. Out of the four oxygens of the Schiff base in $[\mathrm{Cu}^{\mathrm{II}}\mathrm{L}^2\mathrm{Li}^{\mathrm{I}}(\mathrm{H_2O})]^+$, one phenoxo and one methoxy are coordinated to lithium(I), which is also coordinated to one monodentate and one bridging water oxygen to afford a four-coordinate environment.

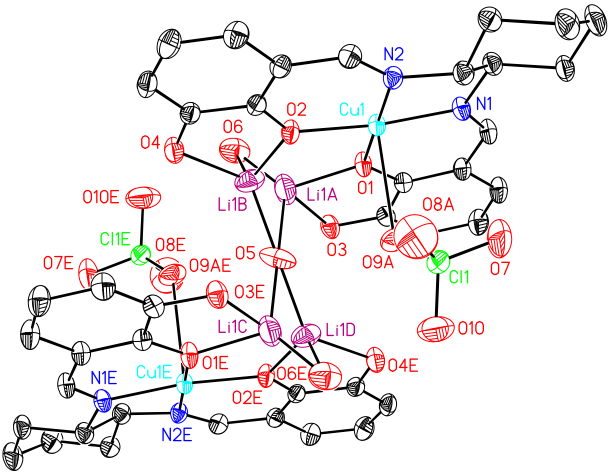

Figure 9. Crystal structure (30% thermal ellipsoids) of $[\{\mathrm{Cu}^{\mathrm{II}}\mathrm{L}^2\mathrm{Li}^{\mathrm{I}}(\mathrm{H_2O})\}_2(\mu\text{-}\mathrm{H_2O})](\mathrm{ClO_4})_2$ (**9**). Hydrogens, methoxy carbons, and two perchlorates are omitted for clarity. Both sites of the disordered lithium(I) center are shown, while one (O8B) of the two sites of one disordered perchlorate oxygen and two (O9B and O9C) of the three sites of the second disordered perchlorate oxygens are omitted for clarity. Symmetry codes: C, D and E, 1 − x, 2 − y, 2 − z.

Table 2. Comparison of bond lengths (Å) and angles (°) of the environment of the second metal center in **1**–**9**.

Compound No.	M–O(Phenoxo)	M–O(Methoxy)	M–H_2O	M–MeCN	M–MeCoMe	M–Perchlorate	M–Chloride	Bond angles around second metal ion	Phenoxo bridge angles
$Cu^{II}Na^{I}$ (**1**)	2.3459(19), 2.366(18)	2.599(2), 2.642(2)		2.483(3)		2.498(12), 2.544(3)		53.0(4)–170.68(7)	103.71(7), 104.77(7)
$Cu^{II}K^{I}$ (**2**)	2.703(18), 2.710(17)	2.736(2), 2.790(2)			2.975(3)	2.866(13) 2.081(14)		41.0(4)–161.82(7)	106.69(7), 107.05(7)
$Cu^{II}Zn^{II}$ (**3**)	2.070(18), 2.146(18)						2.056(9), 2.210(9)	72.98(7)–121.57(4)	100.47(8), 103.47(8)
$Cu^{II}{}_2Na^{I}$ (**4**)	2.422(4)–2.469(5)	2.652(5)–2.724(5)						59.01(13)–175.54(18)	103.40(17)–105.74(18)
$Ni^{II}{}_2K^{I}$ (**5**)	2.749(4)–2.780(4)	2.649(4)–2.685(4)						53.66(12)–170.28(14)	109.74(17)–110.90(16)
$Cu^{II}{}_2Cs^{I}$ (**6**)	3.093(2)–3.215(2)	3.105(2)–3.229(3)				3.085(6)		47.47(6)–160.06(6)	102.71(8)–104.99(9)
$Ni^{II}{}_2Cs^{I}$ (**7**)	3.054(3)–3.171(3)	3.077(3)–3.305(3)				3.354(6)		47.04(7)–155.82(8)	100.64(11)–106.06(11)
$Cu^{II}{}_2Sr^{II}$ (**8**)	2.571(17), 2.591(16)	2.778(18), 2.947(19)	2.616(2)					54.96(5)–177.75(9)	104.63(7), 105.46(7)
$Cu^{II}{}_2Li^{I}{}_2$ (**9**)	1.912(16), 1.890(13)	2.17(3), 2.07(16)	1.660(16), 1.901(17), 1.859(13), 1.903(15)					78.5(8)–128.7(9), 81.2(5)–123.3(9)	113.9(9), 116.6(5)

The bond distances and angles of the coordination environments of Na^I in **1** and **4**, K^I in **2** and **5**, Zn^{II} in **3**, Cs^I in **6** and **7**, Sr^{II} in **8**, and Li^I in **9** and are listed in tables S1–S9; the ranges of bond lengths and angles are compared in table 2.

Due to being disordered over two sites, bond distances involving lithium(I) center in **9** are less accurate. Yet, the lithium(I)–phenoxo (1.890(13) and 1.912(16) Å) and lithium(I)–water (1.660(16)–1.903(15) Å) bond distances in **9**, having two monophenoxo-bridged $Cu^{II}Li^I$ cores, are shorter than the corresponding bond lengths (2.004–2.024 and 1.983–2.004 Å, respectively) in the diphenoxo-bridged $Cu^{II}Li^I$ fragment of the [2 × 1 + 1 × 2] cocrystals derived from a 3-ethoxysalicylaldehyde-diamine (H_2L^{OEt}) ligand [25,28]. Again, the Cu–phenoxo–Li bridge angles (113.9(9) and 116.6(5)°) and Cu···Li distances (3.204 and 3.234 Å) in **9** are greater than the corresponding parameter values (98.8–102.1° and 2.972–2.992 Å) in the two [2 × 1 + 1 × 2] cocrystals derived from H_2L^{OEt}. The range of bond lengths of the lithium(I)–methoxy bond, which has no analog (Li^I–methoxy or Li^I–ethoxy) in systems derived from H_2L^{OMe} or H_2L^{OEt} compartmental ligands, is 2.07(16)–2.17(3) Å. The O–Li–O angles in the $Cu^{II}Li^I$ core in the [2 × 1 + 1 × 2] cocrystals derived from H_2L^{OEt} vary from 77.8–148.8° for one complex and 73.6–149.7° for another, while the O–Li–O angle range in **9** varies in a narrower range, 78.5(8)–128.7(9)°. However, the coordination environment of lithium(I) in all three complexes cannot be modeled by any regular or distorted geometry.

In both $Cu^{II}Na^I$ compound **1** and $Cu^{II}_2Na^I$ **4**, the sodium–phenoxo (2.3459(19)–2.366(18) Å in **1**, 2.422(4)–2.469(5) Å in **4**) bond distances are smaller than the sodium–methoxy (2.599(2)–2.642(2) Å in **1**, 2.652(5)–2.724(5) Å in **4**) bond lengths. In **1**, values of the bond distances involving sodium with chelating perchlorate oxygens (2.498(12) and 2.544(3) Å) and acetonitrile nitrogen (2.483(3) Å) lie between the values of sodium–phenoxo and sodium–methoxy bond lengths. All bond distances lie in usual ranges [14–16], [24–28].

As in **1** and **4**, the similar relative values of the phenoxo and methoxy bond lengths are observed in $Cu^{II}_2Sr^{II}$ **8**, strontium–phenoxo bond lengths are 2.571(17) and 2.591(16) Å, while two strontium–methoxy bond distances are 2.778(18) and 2.947(19) Å. The strontium–water bond length (2.616(2) Å) lies between bond lengths involving phenoxo and methoxy moieties.

In $Cu^{II}_2Cs^I$ **6**, ranges of cesium–phenoxo (3.093(2)–3.215(2) Å) and cesium–methoxy (3.105(2)–3.229(3) Å) bond distances are similar. The range of cesium–methoxy bond lengths (3.077(3)–3.305(3) Å) is slightly wider than cesium–phenoxo (3.054(3)–3.171(3) Å) bond distances in $Ni^{II}_2Cs^I$ **7**. However, the expected trend of bond distances, cesium–methoxy > cesium–phenoxo, is not observed in these complexes; some cesium–phenoxo bond lengths are longer than some cesium–methoxy bond distances and vice versa. However, the ranges of both types of bond distances are in the ranges observed in 3d–cesium compounds derived from H_2L^{OMe}/H_2L^{OEt} [14,28]. While the value of the cesium–perchlorate bond distance, 3.085(6) Å, in **6** lies in between values of other bond distances, the cesium–perchlorate bond in **7** is the longest bond (3.354(6) Å) in this compound.

In previously published work, 3d–potassium(I) compounds of varying nuclearity and dimensionality derived from H_2L^{OMe}/H_2L^{OEt}, the ranges of potassium–phenoxo and potassium–methoxy/ethoxy bond distances are 2.641–2.901 and 2.727–3.210 Å, respectively [14,17–19], [24–26]. Potassium–phenoxo (2.703(18)–2.710(17) Å) and potassium–methoxy (2.736(2)–2.790(2) Å) bond distances in **2** and the potassium–phenoxo (2.749(4)–2.780(4) Å) bond distances in **5** lie in the usual ranges. In contrast, the potassium–methoxy (2.649(4)–2.685(4) Å) bond distances in $Ni^{II}_2K^I$ **5** are smaller than the usual range. In fact, all potassium–phenoxo bond distances in **5** are longer than all potassium–methoxy bond distances. Not only in 3d–potassium(I) but in most of the homo/heterometallic systems derived from H_2L^{OMe}/H_2L^{OEt}, bond distances involving the metal ion in the O_4 compartment with phenoxo ligand are smaller than the methoxy/ethoxy. In some rare cases [14] including **6** and **7**, some metal–phenoxo bond distances are in the range of or slightly longer than some metal–methoxy bond distances. That all metal–phenoxo bond distances are longer than all metal–methoxy bond distances, as observed in **5**, is a new and interesting observation. The potassium–acetone bond distance (2.975(3) Å) in **2** is significantly longer than other bond distances in this molecule.

As expected, zinc–chloride bond distances (2.056(9) and 2.210(9) Å) are longer than zinc–phenoxo bond lengths (2.070(18) and 2.146(18) Å) in $Cu^{II}Zn^{II}$ **3**. The ranges of the O–Zn–O/Cl–Zn–Cl/O–Zn–Cl bond angles lie in the range 72.98(7)–121.57(4)°.

The ranges of bond angles in the coordination environment of the second metal ion (table 2) and the phenoxo bridge angles (100.47(8)–116.6(5)°) in **1–9** lie in the ranges of the similar parameters in related systems derived from H_2L^{OMe}/H_2L^{OEt}. Except the Cu···Zn distance in **3**, copper/nickel… second metal distances in **1–9** follow the expected trend on the basis of ionic radii. The order of ionic radii (Å) is as follows: four-coordinate Li^I (0.59) ≈ four-coordinate Zn^{II} (0.60) < seven-coordinate Na^I (1.12) < eight-coordinate Na^I (1.18) < ten-coordinate Sr^{II} (1.36) < six-coordinate K^I (1.38) < eight-coordinate K^I (1.51) < nine-coordinate Cs^I (1.78). The order of copper/nickel… second metal distances (Å) is as follows: Cu… Zn (3.110 in **3**) < Cu… Li1A/Li1B (3.204/3.234 in **9**) < Cu… Na (3.365 in **1**, 3.433 and 3.448 in **4**) < Cu… Sr (3.584 in **8**) < Cu/Ni… K (3.731 in **2**, 3.823 and 3.838 in **5**) < Cu/Ni… Cs (4.027 and 4.074 in **6**, 3.950 and 4.042 in **7**). As compared in table 2, the bond distances involving the second metal center and phenoxo, water and perchlorate oxygens follow similar trend as the copper/nickel···second metal distances.

Table 3. Geometries (distances in Å and angles in °) of the hydrogen bonds in **1** and **3**–**9**.

Compound no.	D···A/D–H···A	H···A	D···A	D–H···A
2	C9–H9···O9D	2.47	3.40	174.29
	C12–H12···O8E	2.59	3.39	145.18
3	C7–H7···Cl2E	2.69	3.56	156.46
	C9–H9···Cl2E	2.84	3.80	169.08
	C14–H14···Cl1D	2.99	3.85	156.27
4	C14–H14···O11F	2.69	3.57	159.27
	C18–H18···O9D	2.59	3.52	172.15
	C34–H34A···O10E	2.62	3.52	154.12
5	C22–H22C···O11F	2.41	3.36	169.81
	C29–H29···O12G	2.62	3.41	142.44
	C31–H31···O12G	2.44	3.19	137.99
	C34–H34···O9E	2.64	3.55	164.07
	C36–H36···O9E	2.35	3.22	156.48
	C38–H38···O9E	2.61	3.42	144.99
	C44–H44A···O12D	2.64	3.43	140.04
7	C36–H36···O12E	2.57	3.42	151.15
8	O5–H5A···O3E	2.67	3.44	155.23
	O5–H5B···O6D	2.60	3.29	139.55
	O5–H5B···O7D	1.93	2.75	164.49
	C17–H17···O8H	2.49	3.35	154.08
	C21–H21B···O6I	2.53	3.42	153.65
9	C18–H18···O7F	2.40	3.31	166.79

The di/tri/tetranuclear **2–9** are self-assembled by weak attractions, such as hydrogen bonds/cation (K^I)···π/C–H… π interactions. The geometries of all the hydrogen bonds in **2–5** and **7–9** are listed in table 3.

Of the two coordinated chlorides in **3**, Cl2 is a bifurcated donor and interacts with one aromatic C–H (C9E–H9E) and one imine C–H (C7E–H7E), while Cl1 interacts with one imine C–H (C14D–H14D). As shown in figure S1 (Supplementary Material), the three C–H···Cl hydrogen bonds (C9E–H9E···Cl2, C7E–H7E···Cl2 and C14D–H14D···Cl1) result in generation of a 1-D network in **3**.

Neighboring trinuclear molecules in **7** are self-assembled due to one hydrogen bond involving an imine C–H (C36–H36) and one perchlorate oxygen (O12E). Three C–Hπ hydrogen bonds are formed in this compound involving methoxy hydrogens (C21–H21A, C21–H21C, and C44–H44A; H21A···π = 3.029 Å, H21C···π = 3.180 Å and H44A···π = 3.080 Å). While H21C···π is intramolecular, the other two C–H···π interactions are intermolecular and generate the same 1-D chain that is generated by the C36–H36···O12E hydrogen bond (figure 10).

In **9**, one aromatic hydrogen (C18–H18) forms a hydrogen bond with perchlorate oxygen (O7F) of a neighboring molecule resulting in interlinking of the individual tetranuclear molecules to a 1-D self-assembly (figure S2).

There are three C–H···O hydrogen bonds in the structure of **4** involving perchlorate O9D, O10E, and O11F as acceptors and one C(aromatic)–H (C18–H18), one C(aliphatic)–H (C34–H34A), and C44–H44A; H21Aπ = 3.029 Å, H21Cπ = 3.180 Å and H44Aπ = 3.080 Å). While H21Cπ is intramolecular, the other two C–Hπ interactions are intermolecular and gen-

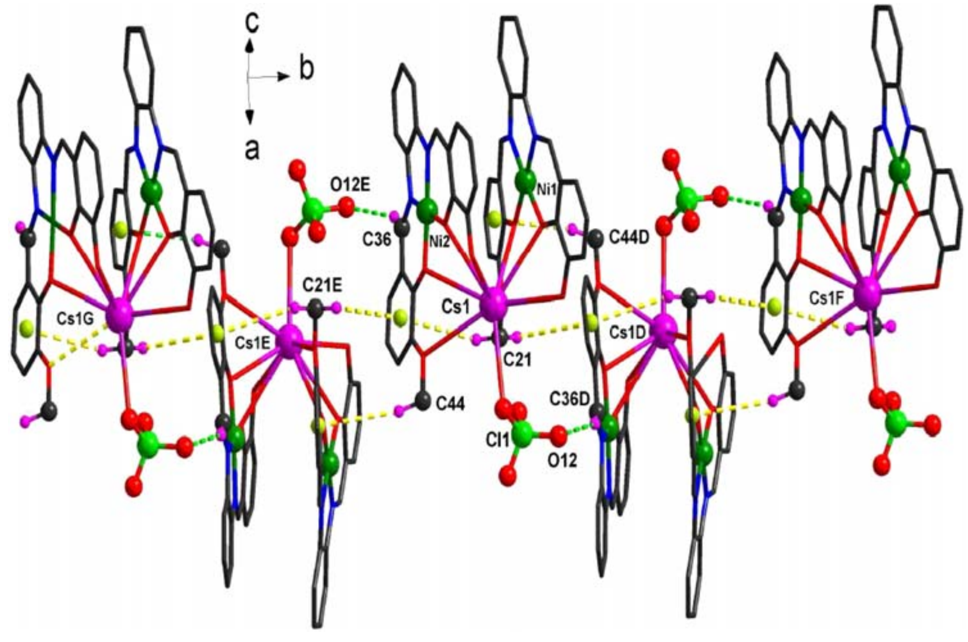

Figure 10. Perspective view of $[(Ni^{II}L^1)_2Cs^I(ClO_4)]\cdot 2H_2O$ (**7**) showing the 1-D topology. Hydrogens and carbons of methoxy moieties, except those participating in hydrogen bonding, two waters and minor occupancy site of the disordered perchlorate are omitted for clarity. Symmetry codes: D, 2 − x, 0.5 + y, 1.5 − z; E, 2 − x, − 0.5 + y, 1.5−z; F, x, 1 + y, z; G, x, − 1 + y, z.

erate the same 1-D chain that is generated by the C36–H36···O12E hydrogen bond (figure 10).

Coordinated water (H_2O5) in **8** forms three hydrogen bonds. One hydrogen (H5B) forms bifurcated hydrogen bonds with two nitrate oxygens (O6D and O7D). The second water hydrogen (H5A) forms a hydrogen bond with the methoxy oxygen (O3E) of a neighboring molecule. The methoxy C–H (C21F–H21BF) hydrogen of this neighboring molecule interacts with the nitrate oxygen O6D, thus O6D is a bifurcated donor. The third nitrate oxygen (O8D) interacts with an aromatic C–H (C17G–H17G) of a different neighboring molecule. As shown in figure 12, the five hydrogen bonds involving one coordinated water and one nitrate result in a 1-D chain; as there are two symmetry related coordinated waters in **8**, the overall result of the hydrogen bonds is to generate a 2-D network (figure 11).

The supramolecular structure of $Cu^{II}K^{I}$ **2** is 3-D (figure 12), generated by two hydrogen bonds, C9–H9···O9D and C12–H12···O8E, and one $K^{I}\cdots\pi$ interaction. As shown in figure 10(a), two neighboring $Cu^{II}K^{I}$ molecules are dimerized due to two symmetry related hydrogen bonds, C9–H9···O9D and C9D–H9D···O9. One such dimer is interlinked with four such dimers due to C12–H12···O8E and its symmetry related three hydrogen bonds, resulting in generation of a 2-D sheet (figure 12(a)). As shown in figure 12(b), one dimer (Cu1K1···Cu1DK1D) of the 2-D sheet in figure 12(a) is interlinked with two other dimers (Cu1K1···Cu1DK1D and Cu1K1···Cu1DK1D) of two different 2-Dsheets due to $K^{I}\cdots\pi$ and its symmetry related interactions. The overall supramolecular structure of **2** is 3-D.

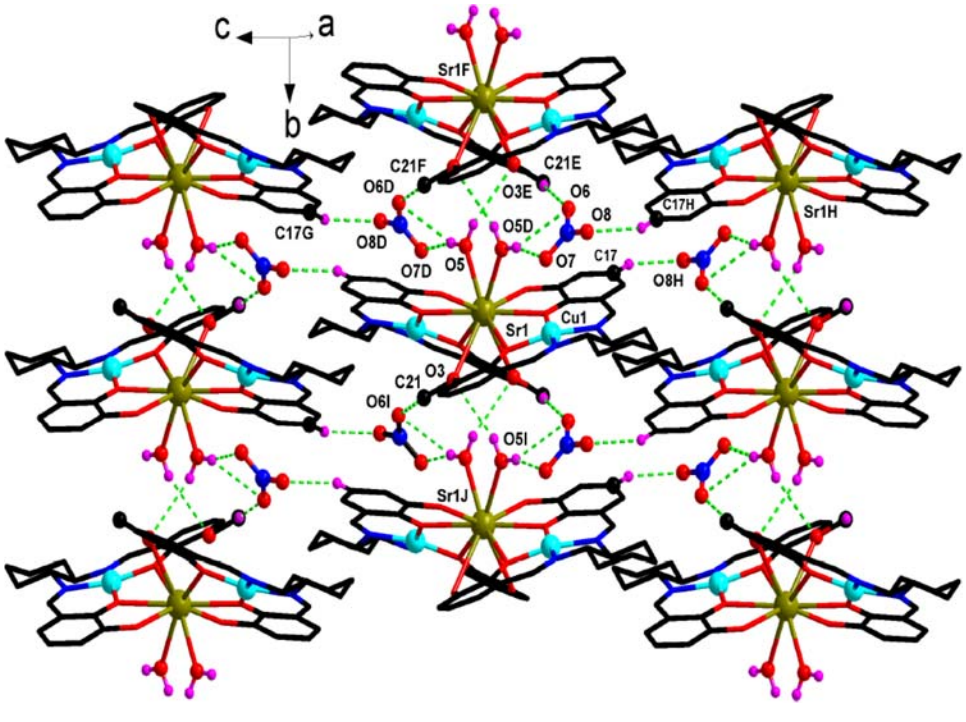

Figure 11. Perspective view of $[(Cu^{II}L^2)_2Sr^{II}(H_2O)_2](NO_3)_2$ (**8**) showing the 2-D network. Hydrogens and carbons of the methoxy moieties, except those participating in hydrogen bonding, are omitted for clarity. Symmetry codes: D, 2 − x, y, 0.5 − z; E, 2 − x, − 1 + y, 0.5 − z; F, x, − 1 + y, z; G, x, 1 − y, 0.5 + z; H, 2 − x, 1 − y, − z; I, 2 − x, 1 + y, 0.5 − z; J, x, 1 + y, z.

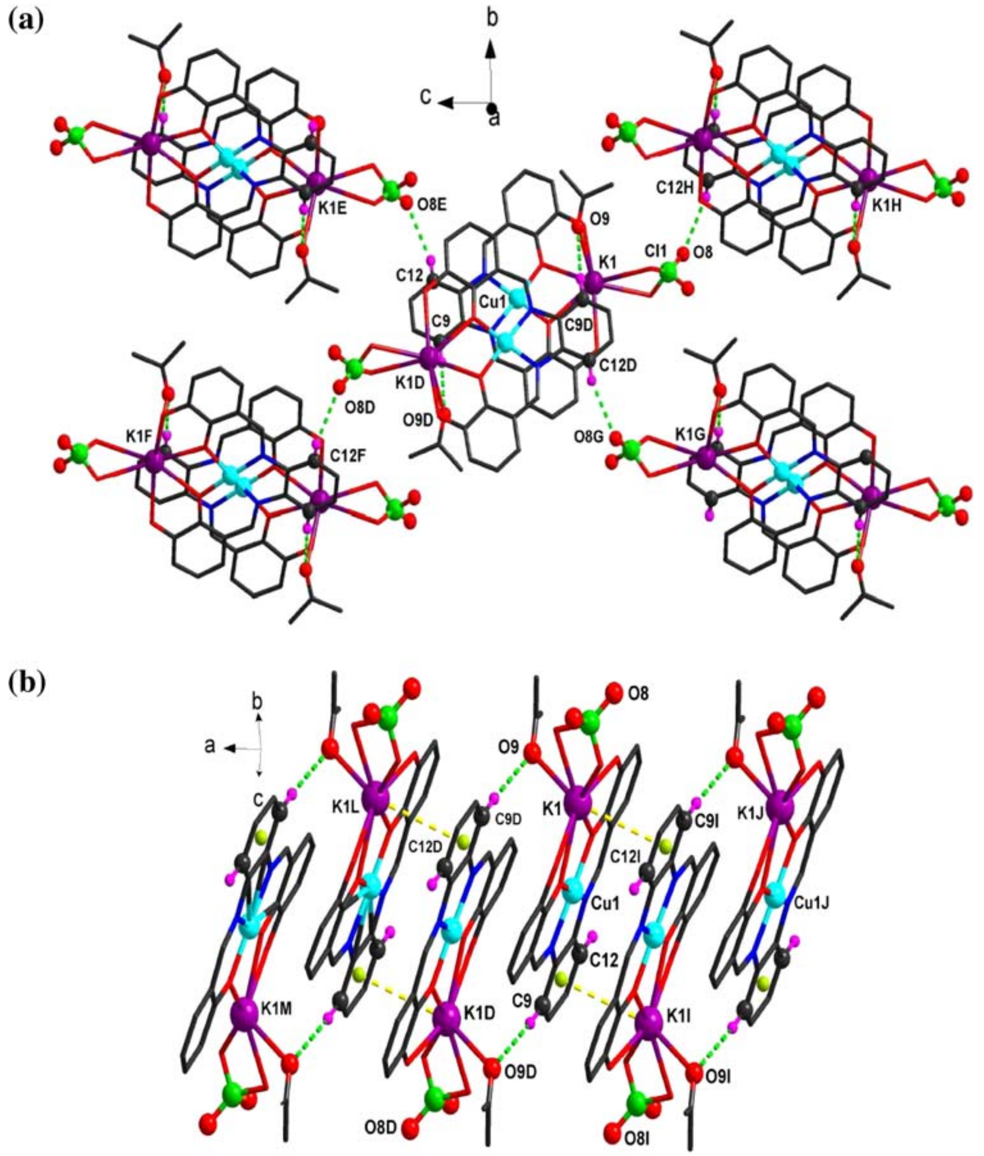

Figure 12. (a) Perspective view showing the dimers of the dinuclear units formed by C9–H9· · ·O9D hydrogen bond and the interlinking of these dimers to a 2-D sheet by C12–H12···O8E hydrogen bond in $[Cu^{II}L^1K^I(ClO_4)(CH_3COCH_3)]$ (**2**). (b) Perspective view to show the interlinking of a dimer of a 2-D sheet in figure 12(a) with two other similar dimers, the latter of which belong to two other 2-D sheets by a $K^I \cdots \pi$interaction to add the third dimensionality of the structure and thus a 3-D topology is formed. Symmetry codes: D, 1 – x, – y, 2 – z; E, x, 0.5 – y, 0.5 + z; F, 1 – x, 0.5 + y, 2.5 – z; G, 1 – x, – 0.5 + y, 1.5 z; H, x, 0.5 – y, – 0.5 + z; I, – x, – y, 2 – z; J, – 1 + x, y, z; L, 1 + x, y, z; M, 2 – x, – y, 2 – z.

The individual trinuclear units in **5** are self-assembled to a 3-D network which may be considered as a combination of two, 2-D sheets shown in figure S4. The following five hydrogen bonds are common in both these sheets: three C(aromatic)–H· · ·O(perchlorate) hydrogen bonds (C31–H31···O12G, C34–H34···O9E, C38–H38···O9E), two C(imine)–H···O(perchlorate) hydrogen bonds (C29–H29···O12G and C36–H36···O9E). Each of the two sheets in figures S4 and S5 is formed due to additional contribution of one of the two different C(methoxy)–H···O hydrogen bonds, C22–H22C···O11F in one case (figure S4) and C44–H44A···O12D for the second case (figure S5).

3.3. *Comparison of the structure and topology of the title compounds with the literature*

Derived from H_2L^{OEt} (3-ethoxysalicylaldehyde-diamine), a few two-component copper(II)–sodium(I) and one three-component nickel(II)–sodium(I) cocrystals of mononuclear and dinuclear or mononuclear, dinuclear and trinuclear units have been reported [24–27]. In addition to cocrystals, a few discrete dinuclear $Cu^{II}Na^{I}/Ni^{II}Na^{I}$ and one trinuclear $Cu^{II}Na^{I}Cu^{II}$ compounds are also known [26,28]. Regarding 3d–sodium(I) systems derived from H_2L^{OMe} (3-methoxysalicylaldehyde-diamine), no cocrystal is known but a few discrete dinuclear and trinuclear compounds have been reported [14–16]. The dinuclear compound $[Cu^{II}L^2Na^{I}(ClO_4)(CH_3CN)]$ (**1**) and trinuclear compound $[(Cu^{II}L^1)_2Na^{I}](ClO_4)\cdot CH_3COCH_3$ (**4**) are structurally similar to the previously reported dinuclear and trinuclear 3d–sodium(I) compounds derived from H_2L^{OMe} or H_2L^{OEt}.

Two interesting examples of double-decker–triple-decker octametallic $Cu_5^{II}K_3^{I}$ cocrystals derived from H_2L^{OEt} are known [24,25]. One dinuclear $Cu^{II}K^{I}$ and one dinuclear $Cu^{II}K^{I}$ based 1-D polymer derived from such ligands are also known [25]. In the H_2L^{OMe} family, the following species are known: one triple-decker pentanuclear $Ni_3^{II}K_2^{I}$ compound [14]; one dinuclear $Cu^{II}K^{I}$ based polymer in which the copper(II) centers of adjacent molecules are bridged by $[Ag(CN)_2]^-$ [17]; one polymeric poly-decker $Ni^{II}K^{I}$ system in which each O_4 compartment is coordinated with two K^{I} centers [14]; a few dinuclear $Mn^{III}K^{I}$ or trinuclear $Mn^{III}K^{I}Mn^{III}$ based polymers in which the manganese(III) centers of adjacent di/trinuclear units are interlinked by hexacyanometalates [18,19]. Thus, the dinuclear $Cu^{II}K^{I}$ compound $[Cu^{II}L^2K^{I}(ClO_4)(CH_3COCH_3)]$ (**2**) is the only discrete dinuclear 3d–K^{I} system in the H_2L^{OMe} family and only the second such example for both the H_2L^{OMe} and H_2L^{OEt} families. On the other hand, the trinuclear $Ni^{II}K^{I}Ni^{II}$ compound $[(Ni^{II}L^2)_2K^{I}](ClO_4)$ (**5**) is the sole example of a discrete non-sandwiched oligonuclear 3d–potassium(I) system in the H_2L^{OEt}/H_2L^{OMe} families.

For 3d–Cs^{I} compounds derived from H_2L^{OEt}, one double-decker $Ni^{II}Cs^{I}Ni^{II}$ system is known [28]. In the H_2L^{OMe} family, three 3d–cesium(I) compounds are known: (i) one double-decker $Ni^{II}Cs^{I}Ni^{II}$ system [14]; (ii) one double-decker $Ni^{II}Cs^{I}Ni^{II}$ based 1-D polymer in which Cs^{I} centers of adjacent molecules are interlinked by bridging I_3^- [14]; (iii) a poly-decker polymeric $Ni^{II}Cs^{I}$ system in which each O_4 compartment is coordinated with two Cs^{I} centers [14]. The double decker $Cu^{II}Cs^{I}Cu^{II}$ and $Ni^{II}Cs^{I}Ni^{II}$ compounds $[(Cu^{II}L^2)_2Cs^{I}(ClO_4)]\cdot 2CH_3CN$ (**6**) and $[(Ni^{II}L^2)_2Cs^{I}(ClO_4)]\cdot 2H_2O$ (**7**) are thus among only a few examples of 3d–Cs^{I} systems derived from H_2L^{OEt}/H_2L^{OMe}.

One dinuclear $Cu^{II}Zn^{II}$ and one trinuclear $Zn^{II}Cu^{II}Zn^{II}$ compounds [20,21], derived from H_2L^{OMe}, and one dinuclear–mononuclear ($Cu^{II}Zn^{II}$–$2Cu^{II}$) cocrystal [29], derived from a H_2L^{OEt}, have been previously reported. The zinc(II) center in $[Cu^{II}L^1Zn^{II}Cl_2]\cdot CH_3CN$ (**3**) and in the previously reported $Cu^{II}Zn^{II}$ cores is four-coordinate and adopts similar distorted tetrahedral geometry.

Two 3d–lithium(I) compounds, both of which are dinuclear–mononuclear ($Cu^{II}Li^{I}$–$2Cu^{II}$) cocrystals, derived from H_2L^{OEt}, have been previously reported [25,28], while there is no example of a 3d–lithium(I) system in the H_2L^{OMe} family. Thus the tetranuclear

$Cu^{II}Li^{I}Li^{I}Cu^{II}$ **9** is the sole example of a 3d–lithium(I) system in the H_2L^{OMe} family. Again, although Li^{I}(μ-water)Li^{I} is a well-known moiety [38], two phenoxo-bridged 3d–Li^{I} dinuclear units bridged by water, as observed in $[\{Cu^{II}L^{1}Li^{I}(H_2O)\}_2(\mu\text{-}H_2O)](ClO_4)_2$ (**9**), is a new type of system.

Although there are a few 3d–magnesium(II)/calcium(II)/barium(II) compounds derived from H_2L^{OEt} [25,29] and a few 3d–calcium(II) compounds derived from H_2L^{OMe} [22], $[(Cu^{II}L^{1})_2Sr^{II}(H_2O)_2](NO_3)_2$ (**8**) is the sole example of a 3d–strontium(II) system derived from H_2L^{OMe}/H_2L^{OEt}.

4. Conclusions

The Schiff bases are useful for designing coordination compounds with interesting structural, magnetic, biomimetic, electrochemical, and photophysical properties [39–46]. The present study designs Schiff base compounds having interesting structural aspects. The major outcomes in line with our aims may be summarized as follows: (i) the only example of a 3d–strontium(II) compound derived from H_2L^{OMe}/H_2L^{OEt}; (ii) the only example of a 3d–lithium(I) compound derived from H_2L^{OMe}; (iii) the only example of a non-sandwiched oligonuclear 3d–potassium(I) compound derived from H_2L^{OMe}/H_2L^{OEt}; (iv) all metal–phenoxo bond distances are longer than the metal–methoxy bond distances in a system; and (v) observation of $C\text{–}H\cdots\pi$ and, more interestingly, of cation $(K^{I})\cdots\pi$ interactions.

Supplementary material

Figures S1–S5, Tables S1–S9, and crystallographic data in cif format for **1–9**. Crystallographic information is available (CCDC reference numbers: 868412, 868414, 868419, 868413, 868415, 868416, 868417, 868418 and for 868411 for 1-9) from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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